

Name	Index Number	Form Class	Tutorial Class	Subject Tutor
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ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY
Higher 2

9729/03

Paper 3 Free Response

30 August 2021
2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS CAREFULLY

Write your name, index number, form class, tutorial class and subject tutor's name on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

Section A Answer all the questions.

Section B Answer one question.

The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [] at the end of each question or part question.

Section	Question No.	For Examiner's Use
		Marks
A	1	
	2	
	3	
	4	
B		
Presentation of answers		
	TOTAL: 80 m	

This document consists of **31** printed pages and **1** blank page.



Section A

Answer **all** the questions in this section.

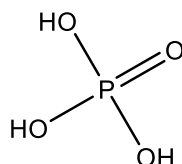
- 1 (a)** Describe the reactions, if any, when separate samples of the oxides Na_2O , Al_2O_3 and P_4O_{10} are added to water. Write equations where appropriate and suggest the pH of any aqueous solution formed.

[4]

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- [2]

The structural formula of phosphoric acid is shown below.



Two molecules of phosphoric acid can undergo a condensation reaction producing diphosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$, and water. The reaction involves an $-\text{OH}$ group from each H_3PO_4 molecule forming an oxygen bridge between the two phosphoric acid units.

- [1]

- [1]

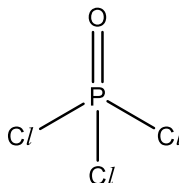
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- (c)** Phosphorus pentachloride can be used to convert alcohols into chloroalkanes. For example,



Phosphoryl chloride, POCl_3 , is formed as a side-product.

- (i) The structure of POCl_3 is shown below.



As there are four bond pairs and zero lone pairs on the phosphorus atom, VSEPR theory predicts that Cl-P-Cl bond angle is 109.5° . However, based on experimental evidence, the actual bond angle is only 103° . Suggest a reason why the actual bond angle is smaller than the predicted one.

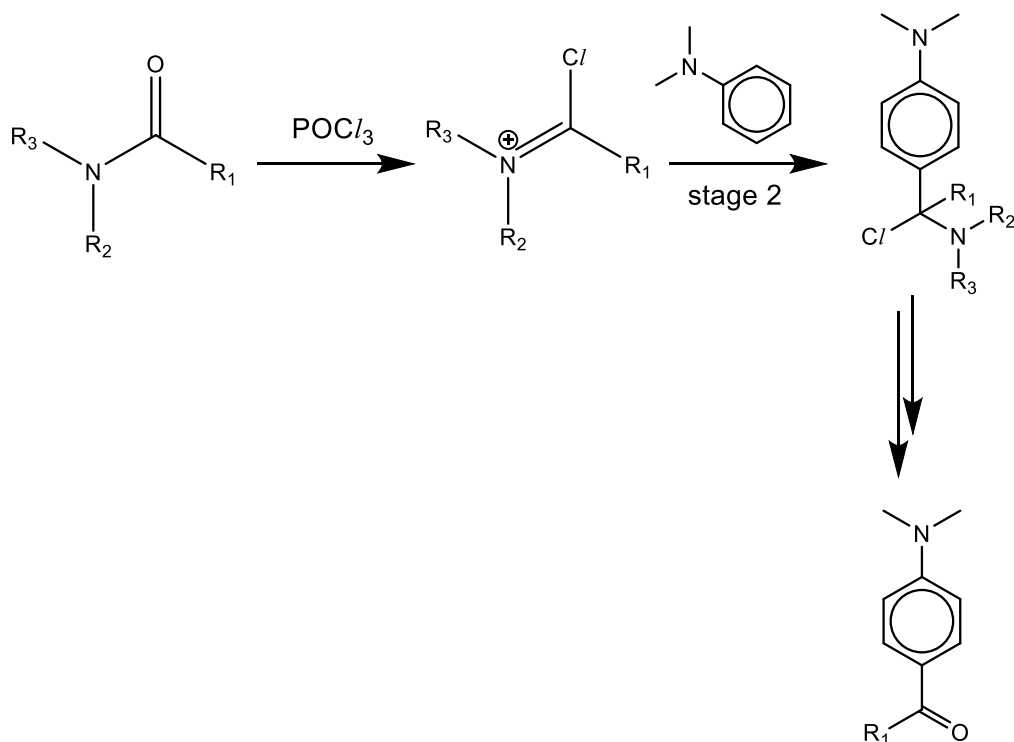
[1]

- (ii) Phosphoryl chloride can be synthesised by reacting PCl_5 with ethanedioic acid in equimolar amounts. Two moles of HCl is formed per mole of PCl_5 , together with two other gases, one polar, the other non-polar. Identify the polar gas and the non-polar gas and write a balanced equation of this reaction.

[3]

[illegible]

- (c) (iii) The Vilsmeier–Haack reaction involves the use of phosphoryl chloride and a substituted amide to produce an aryl aldehyde or aryl ketone. An example of the Vilsmeier–Haack reaction is shown below.



The mechanism of stage 2 consists of two steps. Using curly arrows and showing all relevant charges, propose the mechanism for stage 2.

[3]

[Total: 15]

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- 2 Magnesium reacts with pure nitrogen to form magnesium nitride, Mg_3N_2 , which can be considered as a possible intermediate in the 'fixing' of nitrogen to make ammonia-based fertilisers.



Nitrogen is an essential macronutrient needed by all plants to thrive. It is an important component of many structural, genetic and metabolic compounds in plant cells.

- (a) When water is added to Mg_3N_2 , a colourless gas which turns moist red litmus paper blue is produced.

This gas reacts with chlorate(I) ion, ClO^- in a 2:1 mole ratio to form a colourless liquid **A** with empirical formula NH_2 . The reaction of **A** with sulfuric acid in a 1:1 mole ratio produces a salt **B**, $\text{O}_4\text{N}_2\text{SH}_6$, which contains one cation and one anion per formula unit.

Explain the role of the nitride ion when water was added to Mg_3N_2 .

Deduce the structures of compounds **A** and **B**.

[3]

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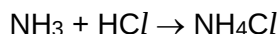
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$$\text{NH}_2\text{CONH}_2 + 2\text{OH}^- \rightarrow 2\text{NH}_3 + \text{CO}_3^{2-}$$


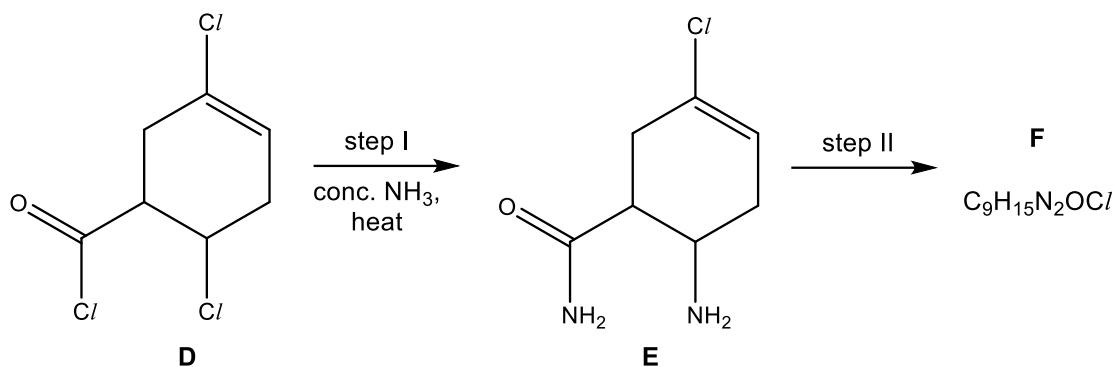
(i) Calculate the percentage by mass of nitrogen in the urea-containing fertiliser. [2]

A molecule of UHP is made up of one molecule each of hydrogen peroxide and urea held together by hydrogen bonding in a seven-membered ring. Draw a fully labelled diagram of a molecule of UHP.

[2]

[illegible]

(c) Ammonia is used in the synthesis of **F** from **D** as shown below.



- (i) Give the reagents and conditions for step II and hence suggest the structure of **F**. [2]
- (ii) One of the three chlorine atoms in **D** is inert towards hot concentrated NH_3 . Explain why this is so. [1]
- (iii) Suggest a simple chemical test to differentiate between **D** and **E**. State the observations. [2]

[Total: 12]

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- 3 Calcium ethanedioate (CaC_2O_4) is the primary constituent of the common kidney stones, and is believed to form due to inappropriate diets.

Napoleon Bonaparte and Napoleon III were suffering from bladder stones and had severe symptoms, probably affecting their military decisions. Today, historians still debate over what might have happened in his Russian campaign in 1812 if Napoleon Bonaparte had not had a bladder stone. Similarly, the course of European history might have changed if Napoleon III was treated with modern surgical techniques during the Franco-Prussian War of 1870.

- (a) The value of the solubility product of calcium ethanedioate is 2.32×10^{-9} at 25°C .
- (i) Write an expression for the solubility product of calcium ethanedioate and state its units. [2]
- (ii) Calculate the solubility of calcium ethanedioate in pure water at 25°C . [1]
- (iii) Calculate the solubility of calcium ethanedioate in a 0.30 mol dm^{-3} of calcium nitrate at 25°C . [2]

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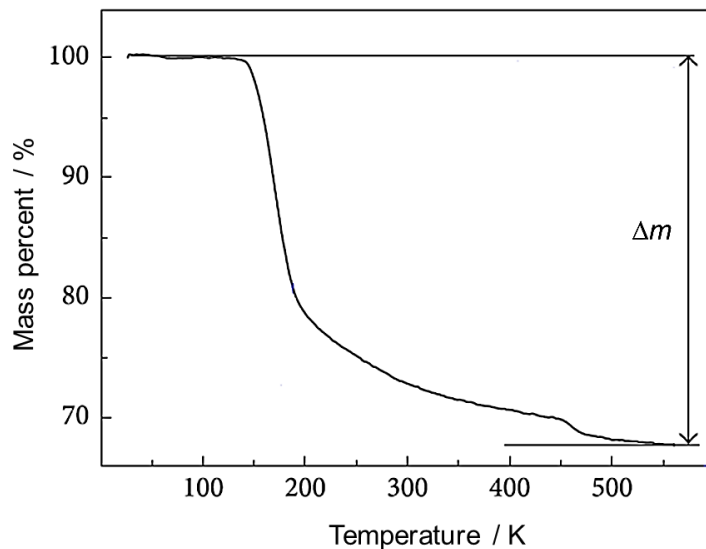
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- (b)** Calcium ethanedioate decomposes at a higher temperature than magnesium ethanedioate. Explain this difference in their decomposition temperatures.

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- (c) Thermogravimetric analysis (TGA) is a technique where the mass of a sample in a controlled atmosphere is recorded as a function of temperature as the temperature of the sample is increased.

A sample of lithium pentaborate pentahydrate ($\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$) was subject to TGA and the graph obtained is shown below. The relative molecular mass of $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$ is 278.9.



- (i) Suggest an explanation, supported with relevant calculations, for the loss in mass (Δm) of $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$ observed in the graph. [2]
- (ii) The sample of $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$ used in (i) was synthesised from Li_2O , B_2O_3 and H_2O in the laboratory. Deduce the molar ratio of $\text{Li}_2\text{O} : \text{B}_2\text{O}_3 : \text{H}_2\text{O}$ used to produce a pure sample of $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$. [1]
- (iii) Aqueous sodium hydroxide can be used to react with B_2O_3 to determine its actual amount in the sample.

Given that B_2O_3 and Al_2O_3 have similar reactions with aqueous sodium hydroxide under appropriate conditions, write a balanced equation for the reaction between B_2O_3 and aqueous sodium hydroxide. [1]

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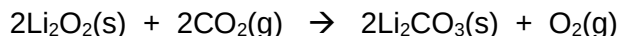
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(d) Lithium peroxide, Li_2O_2 , is a white solid.

- (i) Li_2O_2 has been used to remove CO_2 from the atmosphere in spacecraft. It reacts with carbon dioxide according to the equation shown below. This is a disproportionation reaction.



Explain the term *disproportionation* with reference to the changes in the oxidation numbers of the appropriate element in the above reaction.

[2]

- (ii) When a precipitate is formed, $\Delta G_{\text{ppt}}^\ominus$ is given by the following equation.

$$\Delta G_{\text{ppt}}^\ominus = 2.303 RT \log_{10} K_{\text{sp}}$$

The value of the K_{sp} of lithium carbonate is 8.15×10^{-4} at 298 K.

Use the equation given above to deduce if lithium carbonate is soluble in water at 298 K. Explain your answer.

[2]

[Total: 15]

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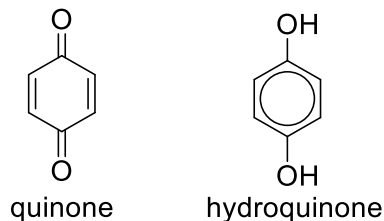
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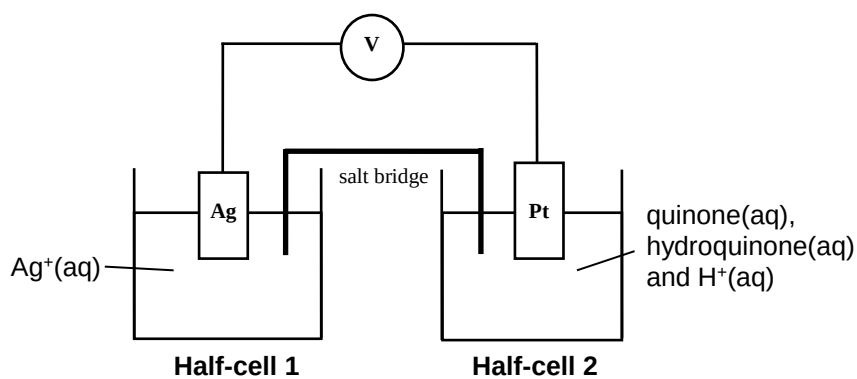
4 The use of the *Data Booklet* is relevant for this part.

A quinhydrone half-cell comprises a platinum electrode immersed in a solution which is prepared by dissolving a mixture of quinone and hydroquinone in acid.



The standard reduction potential, $E^\ominus$, of the quinone-hydroquinone system is +0.70 V.

An electrochemical cell, which consists of a standard quinone-hydroquinone half-cell and a standard Ag^+/Ag half-cell, was set up.



- (a) (i) Write the half-equations of the reactions which occur at the cathode and anode. [2]
- (ii) State the reading on the voltmeter, when the above electrochemical cell is set up. [1]

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- (a) (iii) Calculate the standard Gibbs' free energy change of this electrochemical cell. [2]
- (iv) Some aqueous ammonia was added in excess to the Ag^+/Ag half-cell. Predict the effect of this change on the reading on the voltmeter. You are to include the structural formula of the complex formed in your answer. [4]

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- (b) Blattellaquinone is a sex pheromone of the German cockroach. It is secreted by females to attract male cockroaches.

The molecular formula of blattellaquinone is $C_{12}H_{14}O_4$. As the suffix suggests, it is a quinone derivative.

On reaction with lithium aluminium hydride in dry ether, 3-methylbutan-1-ol and **Q** (molecular formula $C_7H_{10}O_3$) are formed.

Using the structures on page 14, deduce the structures of blattellaquinone and **Q**.

[2]

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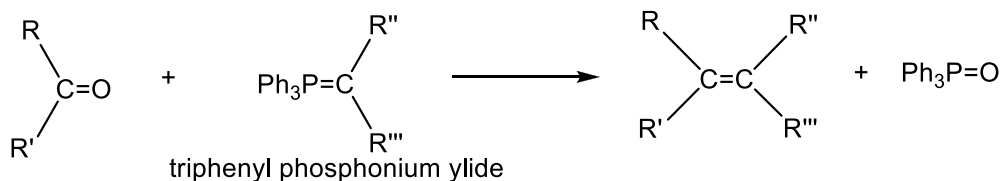
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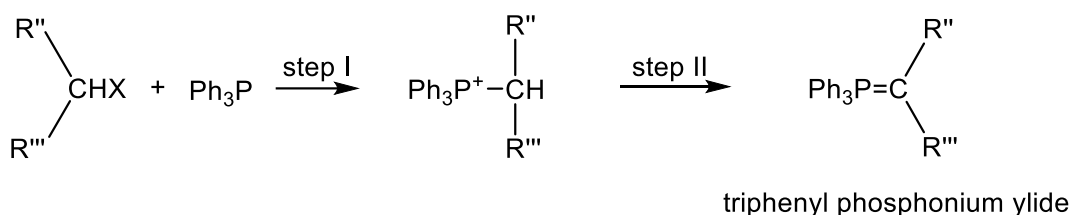
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- (c) For alkenes to be useful starting materials for synthesis of organic chemicals, it is important to synthesise alkenes with the carbon-carbon double bonds at specific positions with no ambiguity.

In 1954, a German chemist Georg Wittig reported a method of synthesising alkenes from ketones and aldehydes using a reagent known as triphenyl phosphonium ylide, $\text{Ph}_3\text{P}=\text{CRR}'$, which is also known as the Wittig reagent. The phenyl group is abbreviated as 'Ph'.



Wittig reagents can be produced by the reaction of alkyl halides with triphenylphosphine in the following two-step processes.



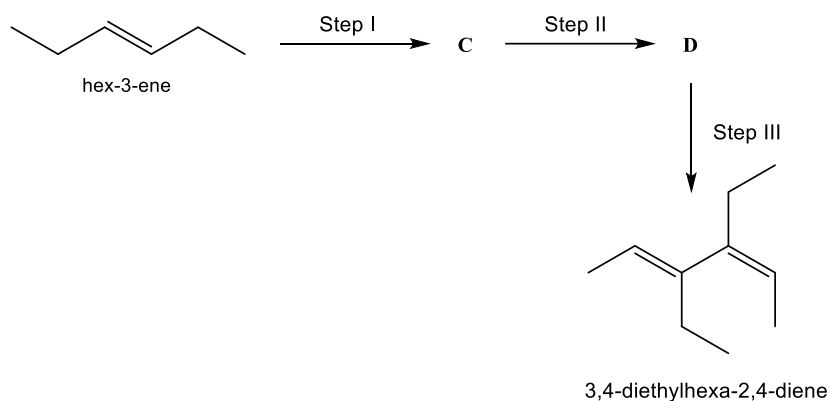
- (i) Identify the types of reaction in steps I and II.

[2]

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- (c) (ii) The conversion of hex-3-ene to 3,4-diethylhexa-2,4-diene involves three steps. Steps I and II are oxidation reactions. A Wittig reagent is used in one of the steps.



Deduce the structures of the intermediates **C** and **D** and the Wittig reagent involved.

[3]

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- (iii) State the number of stereoisomers 3,4-diethylhexa-2,4-diene exists in. [1]

- (iv) Draw the skeletal formula of the constitutional isomer of hex-3-ene in which all the carbon atoms are sp^3 hybridised, and forms only one mono-chlorinated product on reaction with limited chlorine in the presence of ultraviolet light.

[1]

[Total: 18]

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Section B

Answer **one** question from this section.

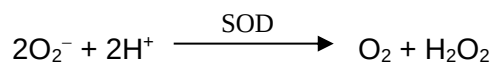
- 5 Copper was the first metal to be worked by man, along with gold and meteoritic iron. This is because these metals were among the few that can be found in a relatively pure form in nature.

(a) Write the electronic configuration of the outermost shell of Cu^+ .

[1]

(b) An example of a copper-containing enzyme is superoxide dismutase (SOD).

It aids in the disproportionation of the strongly oxidising superoxide ion, O_2^- to oxygen and hydrogen peroxide, thereby protecting the body from harm.



The activity of SOD hinges on the active site Cu^{2+} ion which can be reduced to Cu^+ .

By referring to the following $E^\ominus$ data, suggest a mechanism for the catalysis of the disproportionation of O_2^- by SOD.

	$E^\ominus / \text{V}$
$\text{O}_2 + \text{e}^- \rightleftharpoons \text{O}_2^-$	-0.33
$\text{O}_2^- + \text{e}^- + 2\text{H}^+ \rightleftharpoons \text{H}_2\text{O}_2$	+0.89
$\text{SOD-Cu}^{2+} + \text{e}^- \rightleftharpoons \text{SOD-Cu}^+$	+0.42

You may represent the oxidised and reduced forms of the enzyme as SOD-Cu^{2+} and SOD-Cu^+ .

[3]

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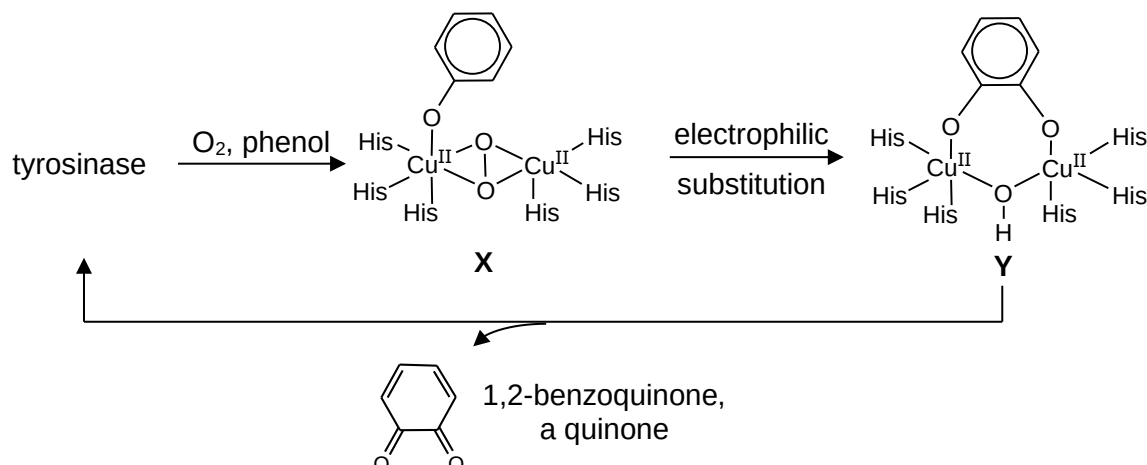
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- (c) Another copper-containing enzyme is tyrosinase which catalyses the oxidation of phenols to quinones. **X** and **Y** are two intermediate species in the catalytic cycle of tyrosinase. The conversion of **X** to **Y** involves an electrophilic substitution mechanism.



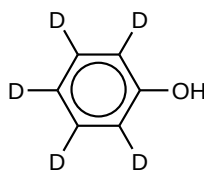
- (i) Experiments were conducted using different phenol substrates and the relative rates of reactions are shown below.

phenol substrate		
relative rate	7.9	0.02

Account for the different relative rates of reactions.

[2]

- (ii) In the phenol substrate **III** below, the hydrogen atoms on the phenyl ring are replaced with deuterium ($D = {}^2_1H$). The bond dissociation energy of the C–D bond is greater than that of the C–H bond.



III

Predict and explain how the relative rate of reaction for substrate **III** would compare to that of substrate **I**.

[1]

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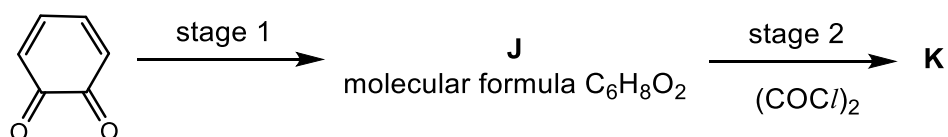
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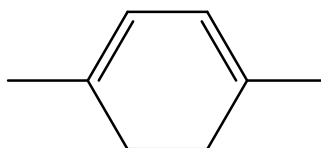
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(d) The quinone product from (c) can undergo the following reaction.



- (i) Suggest the structural formulae of **J** and **K**, given that 2,4-dinitrophenylhydrazine can distinguish between the quinone starting material and **K**. [2]
- (ii) Suggest, in no more than three steps, how butanedioic acid can be obtained from 1,4-dimethylcyclohexa-1,3-diene.



1,4-dimethylcyclohexa-1,3-diene

You are to include the structural formula(e) of all the intermediate(s).

[3]

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- (e) Fehling's solution can be prepared by mixing copper(II) sulfate and aqueous potassium sodium tartrate with aqueous sodium hydroxide.

The condensed structural formula of D-erythrose is $\text{HOCH}_2\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CHO}$.

State what would be observed when a few drops of Fehling's solution is introduced to D-erythrose solution. Write the balanced equation between Fehling's solution and D-erythrose, showing the structure of the organic product.

[3]

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- (f) When fluorine gas is passed over a heated mixture of potassium chloride and copper(II) chloride, a pale green solid, **J**, containing only potassium, copper and fluorine is formed.

When 1.00 g of **J** was reacted with water, 20.4 cm³ of oxygen (measured at 293 K and 1 atm) were evolved and a blue acidic solution was formed. The resulting solution was divided into two equal parts. Titration of one part with 0.100 mol dm⁻³ NaOH required 17.00 cm³ for neutralisation. The other part was electrolysed and 0.108 g of copper metal was deposited at the cathode.

- (i) Calculate the number of moles of oxygen molecules, copper(II) ions and hydrogen ions formed in the reaction with water.

[3]

- (ii) The oxidation state of copper in **J** is +3. Assuming that 1 mol of **J** contains 1 mol of copper atoms, deduce its relative formula mass and hence its formula.

[2]

[Total: 20]

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- 6** Iron is one of the most abundant element found on earth. It comprises about 5.6% of the earth's crust and almost all of the earth's core. It is also commonly found in both humans and plants.

- (a) (i)** Iron exists in many oxidation states.

An oxoanion of iron has the formula FeO_x^{2-} . In acidic conditions, FeO_x^{2-} is a strong oxidising agent and is reduced to Fe^{3+} . In an experiment, a 30 cm^3 of $0.200 \text{ mol dm}^{-3}$ of FeO_x^{2-} completely oxidised 30 cm^3 of $0.600 \text{ mol dm}^{-3}$ of Fe^{2+} to Fe^{3+} . Determine the value of x .

[3]

The most common oxidation states of iron are +2 and +3. Both iron(II) and iron(III) ions form complexes with H_2O and CN^- .

- (ii) Draw a fully labelled diagram to describe how the standard reduction potential of the $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ half-cell can be measured using a standard hydrogen electrode.

[3]

- (iii) By quoting relevant data from the Data Booklet, explain why aqueous iron(III) iodide does not exist while aqueous iron(III) chloride exists.

[2]

- (iv)** In the presence of iron(III) chloride, phenol does not undergo Friedel-Crafts alkylation with halogenoalkanes. This is because the phenol reacts with iron(III) chloride in an acid-base reaction to form a neutral compound. Suggest the structure of this product.

[1]

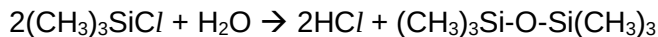
[illegible]

- (b) (i) Write a balanced equation of the reaction between SiCl_4 and water.

[1]

Trimethylsilyl chloride, $(\text{CH}_3)_3\text{SiCl}$, is closely related to SiCl_4 . It is a colourless liquid that is stable in the absence of water.

It reacts with water according to the following equation.



- (ii) The above reaction is slower than the reaction in (i). Give two reasons for the difference in reaction rates.

[2]

- (iii) The bond energy of the Si-C bond is commonly quoted as + 318 kJ mol⁻¹. Using additional data from the *Data Booklet*, calculate the enthalpy change of the above reaction.

[2]

- (iv) The calculated value in (iii) is different from the experimentally determined value. Give a reason for the difference.

[1]

One of the hydrated forms of iron(III) chloride has a molecular formula of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.

Heating hydrated iron(III) chloride does not yield anhydrous iron(III) chloride. Instead, the solid decomposes on heating.

- (v) Anhydrous iron(III) chloride can be obtained by reacting hydrated iron(III) chloride with trimethylsilyl chloride. Write a balanced equation of this reaction.

[1]

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- (c) British astronomer and photographer John Herschel used iron-based reagents to obtain a blue pigment (known as Turnbull's Blue) to develop the blue printing technique in 1842. Now, blue printing can be easily carried out using the photochemical redox chemistry of potassium iron(III) ethanedioate.

The molecular formula of potassium iron(III) ethanedioate is $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3$. Its relative formula mass is 437.1.

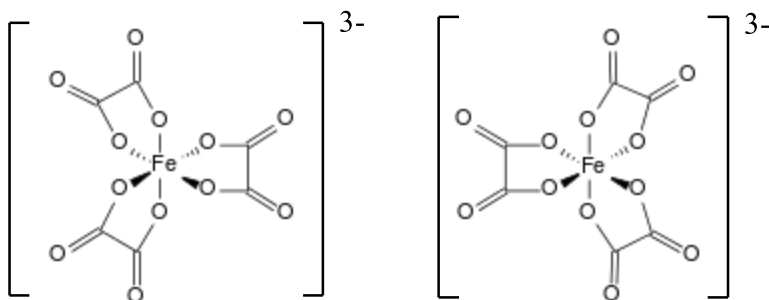
To confirm the molecular formula, 0.250 g of potassium iron(III) ethanedioate sample was added to 25 cm^3 of $4.00 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. After heating this solution, it was titrated with $0.0196 \text{ mol dm}^{-3} \text{ KMnO}_4$ till the light pink colour was obtained. The titration reading was $x \text{ cm}^3$.

After this titration, an excess of zinc powder was added to the same flask that led to effervescence in the solution. When the effervescence subsided, the solution was boiled for fifteen minutes. The flask was cooled to room temperature and was titrated with the same KMnO_4 solution. The titration reading was 5.10 cm^3 .

- (i) Find the value of x .

[3]

- (ii) The anionic complex exists as a pair of enantiomers, as shown below.



State the structural feature of the complex which is responsible for such a phenomenon.

[1]

[Total: 20]

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Additional answer space

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